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Development of a dynamic model for cleaning ultra filtration membranes fouled by surface water

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Abstract

In this paper, a dynamic model for cleaning ultra filtration membranes fouled by surface water is proposed. A model that captures the dynamics well is valuable for the optimization of the cleaning process. The proposed model is based on component balances and contains three parameters that can be determined by a simple experimental protocol that facilitates the possibility of online adaptation of model parameters at frequent intervals. This may be required when process conditions change and/or water quality varies with time. Experiments were performed to test and validate the model.

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Keywords: Membranes; Ultra filtration; Chemical cleaning; Modeling

1. Introduction

Ultra filtration is increasingly used as a technology to purify surface water. UF membranes have high selectivity and are economically attractive. A major drawback, however, is the limitation in performance as a result of fouling. Consequently, frequent cleaning of the membrane is necessary. In the short term, fouling is controlled by means of hydraulic cleanings (backwashes), but in the long term, fouling that cannot be removed by means of backwashes builds up, and treatment of the membrane with chemicals is required. It is expected that cleaning costs can be reduced by means of optimization.

The main objective of this paper is the development of a cleaning model that is suitable for (dynamic) optimization of the chemical cleaning procedure. A three parameter model that describes dynamic behavior of a chemical cleaning procedure is proposed. After construction of the model, a protocol for experimental verification of the model is developed and tested. The model parameters are determined by a nonlinear least squares algorithm using experimental runs. The fitted parameters are consequently used to validate the model for additional experi-

mental runs. It was found that the model describes the cleaning process well.

2. Theory

2.1. Requirements of the model

Chemical cleaning of membranes is widely studied in a qualitative way [1–6]. In these studies, the characterization of fouling and the interactions that occur between fouling, cleaning agent and membrane surface are described in detail.

The number of authors who published on the modeling aspects of chemical cleaning of membranes is limited. Bird [7] developed a microscopic cleaning model for the caustic cleaning of ceramic micro-filtration filters fouled by whey concentrate. Xin et al. [8] constructed similar cleaning models that can be used to predict cleaning rates during the cleaning process of metal surfaces (e.g. heat exchangers) fouled by colloids. Li et al. [9] developed a cleaning model based on cleaning kinetics to predict cleaning efficiency for different cleaning agents that were used to clean polymeric ultra filtration membranes fouled by glutamic components.

Although researchers suggest different physico-chemical mechanisms that can be responsible for the effect of the chem-

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Nomenclature

E	turbidity (FNU)
J	cleaning flux
J^*	reference cleaning flux ($1 \text{ h}^{-1} \text{ m}^{-2}$)
J_{in}	cleaning flux at the inlet ($1 \text{ h}^{-1} \text{ m}^{-2}$)
k'	flushing rate constant (min^{-1})
k''	cleaning rate constant (min^{-1})
n_C	pseudo-stoichiometric coefficient
pH	pH during cleaning
pH*	reference pH
pH _{in}	pH of the cleaning agent at the inlet
ΔP	trans membrane pressure (mbar)
r''_W	cleaning rate (min^{-1})
t	time (min)
t_e	end time (min)

Greek letter

ϵ_∞	cleaning effectiveness at infinite cleaning time
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ical cleaning of the membrane, they generally agree upon the fact, that chemical cleaning can be enhanced by altering (a) the cleaning time, (b) the type of cleaning agent, (c) the cleaning agent concentration, (d) the cleaning temperature, and (e) the cleaning flux.

In order to be suitable for optimization of a chemical cleaning procedure, a cleaning model should meet the following requirements: (a) capture the dynamics of decay of irreversible fouling, (b) incorporate variables that can be used to control/optimize the cleaning procedure, e.g. cleaning flux and cleaning agent concentration and (c) exhibit a simple structure with only few parameters that need to be estimated.

2.2. Model development

The cleaning model presented here is developed in terms of macroscopic component balances. It is assumed that the irreversible fouling on the membrane is converted to unspecified decomposition products as a result of exposure to cleaning chemicals. Irreversible fouling is in this context defined as fouling that cannot be removed by means of hydraulic cleanings. The trans membrane pressure measured during a filtration at a fixed flux with clean water is a good indicator of the fouling status of the membrane. The trans membrane pressure is correlated to the irreversible fouling state $x_W(t)$ according to

$$x_W(t) = \frac{\Delta P(t)}{\Delta P_0} \quad (1)$$

where $\Delta P(t)$ is the trans membrane pressure during cleaning at specified flux and ΔP_0 the trans membrane pressure at the beginning of the cleaning determined by filtration with clean water at a specified flux. A problem, however, is that the trans membrane pressure can only be measured before and after cleaning. For this reason the trans membrane pressure will be used to scale the effectiveness of the cleaning, but the dynamics need to

be monitored by different means, namely by turbidity measurements of the cleaning concentrate. The following relationship is suggested:

$$\frac{\Delta P(t)}{\Delta P_0} = 1 - \epsilon_\infty \frac{\int_0^t E \, dt}{\int_0^{t_e} E \, dt} \quad (2)$$

E is the turbidity measured at the outlet of the membrane unit and t_e is the duration of the chemical cleaning procedure. The integral of the turbidity reflects the ‘amount of irreversible fouling that has been removed’. The integral is normalized to one and scaled by means of the trans membrane pressure based cleaning effectiveness:

$$\epsilon_\infty = \frac{\Delta P_0 - \Delta P_\infty}{\Delta P_0 - \Delta P_m} \quad (3)$$

where $\Delta P_\infty \approx \Delta P(t_e)$ and ΔP_m is the trans membrane pressure of a clean membrane determined at a specified clean water flux. The cleaning effectiveness is the ratio of the decrease in trans membrane pressure during a chemical cleaning procedure and the increase in trans membrane pressure during a production cycle. Fig. 1 shows how trans membrane pressure increases during a production cycle and decreases during chemical cleaning.

The decay of irreversible fouling is described by

$$\frac{dx_W}{dt} = -k' J (x_W - x_{W,\infty}) + r''_W \quad (4)$$

where k' is a flushing rate constant and J is the dimensionless cleaning flux:

$$J = \frac{J_{\text{in}}}{J^*} \quad (5)$$

where J_{in} is the cleaning flux at the inlet and J^* a reference cleaning flux ($=1501^{-1} \text{ h}^{-1} \text{ m}^{-2}$, based on the maximal cleaning flux), $x_{W,\infty}$ is the irreversible fouling state at infinite cleaning time and r''_W is a first order cleaning rate equation, formulated as

$$r''_W = -k'' x_C (x_W - x_{W,\infty}) \quad (6)$$

where k'' is a cleaning rate constant which may be temperature dependent and x_C is the cleaning agent state. Note that the ratio

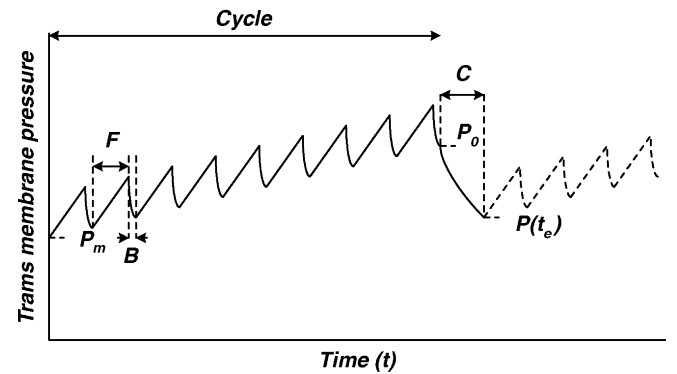


Fig. 1. Representation of a production cycle with a certain number of filtrations (F) and backwashes (B), followed by a chemical cleaning procedure (C). At the beginning of the production cycle the trans membrane pressure measured at a specified clean water flux is ΔP_m . At the end of the production cycle the trans membrane pressure increased to ΔP_0 . After a chemical cleaning procedure, the trans membrane pressure decreased to $\Delta P(t_e)$.

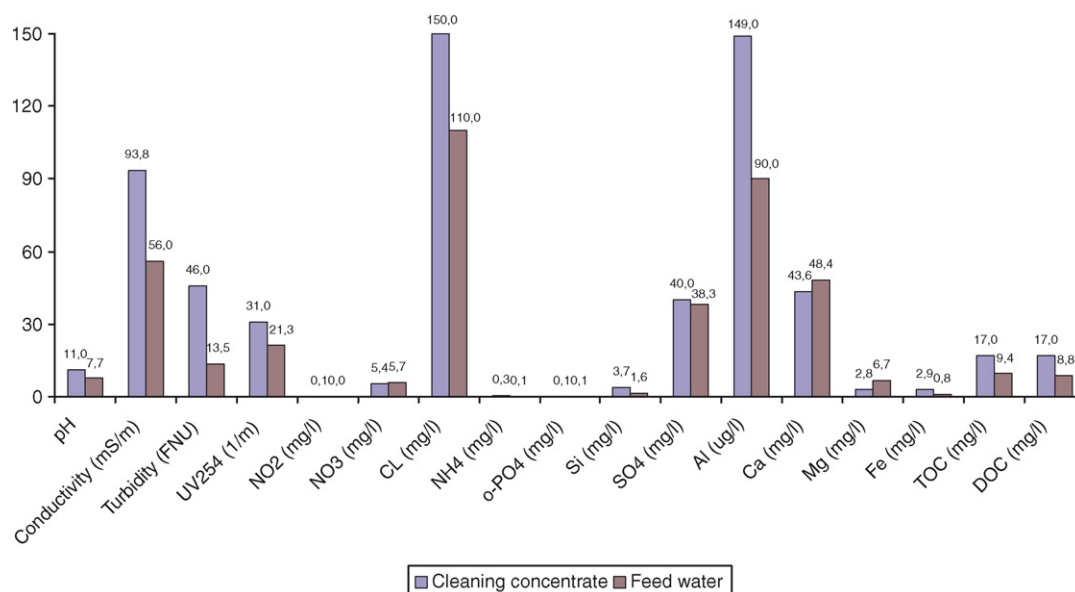


Fig. 3. Feed water and cleaning concentrate composition.

sium), also organic matter is found in higher concentrations in the cleaning concentrate (DOC and TOC). The presence of increased amounts of ammonia and nitrite may indicate removal of microbial content.

Surface water was stored in a 20 l feed tank, which was refreshed every 5 h. Sodium hydroxide was used as a cleaning agent in varying concentrations.

3.2. Procedure

The experimental protocol followed for fouling and cleaning of the membrane is shown in Fig. 4. The experimental protocol followed, has the advantage that it can be executed relatively fast and that it resembles the fouling build-up during conventional operation adequately. The model as proposed has been shown to capture the dynamic behavior during conventional operation well. First a filtration procedure with a flux of $100 \text{ l h}^{-1} \text{ m}^{-2}$ is performed until the temperature corrected trans membrane pressure of the membrane has increased from $\Delta P_m = 350 \text{ mbar}$ to approximately 500 mbar. Subsequently, a backwash procedure is executed, in which a volume of 500 ml permeate is flushed

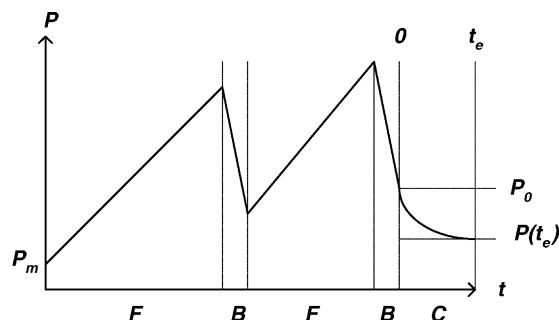


Fig. 4. Followed procedure: filtration (F), backwash (B), flushing with chemicals (C).

back with a flux of $150 \text{ l h}^{-1} \text{ m}^{-2}$. Next, a second filtration procedure is started with a flux of $100 \text{ l h}^{-1} \text{ m}^{-2}$, until a temperature corrected trans membrane pressure of approximately 550 mbar is reached. This filtration is followed by a backwash procedure in which a volume of 500 ml permeate is flushed back with a flux of $150 \text{ l h}^{-1} \text{ m}^{-2}$. Then a volume 1000 ml of sodium hydroxide is flushed through the membrane with a flux of $150 \text{ l h}^{-1} \text{ m}^{-2}$. Different concentrations of sodium hydroxide are used. Concentrations lower than 0.01 M have been shown to be ineffective in cleaning the membrane, while the membrane supplier advises not to use concentrations higher than 0.1 M. We have chosen to vary the concentrations from 0.015 to 0.13 M. At the permeate outlet, the concentrate is collected and pH and turbidity are measured. After the chemical cleaning procedure the remaining chemicals are flushed out of the system with an additional backwash of 500 ml performed at a flux of $150 \text{ l h}^{-1} \text{ m}^{-2}$. Trans membrane pressure is measured before (ΔP_0) and after ($\Delta P(t_e)$) the chemical cleaning procedure by a short filtration at a flux of $100 \text{ l h}^{-1} \text{ m}^{-2}$ with clean water. A typical profile for turbidity and

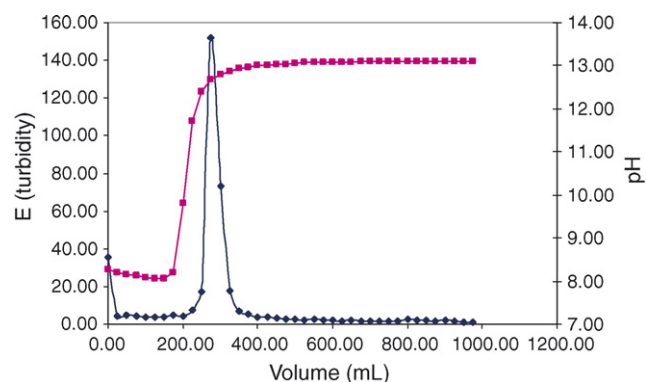


Fig. 5. Typical experimental results. Turbidity (diamond) and pH (square) measured at the outlet during a chemical cleaning procedure.

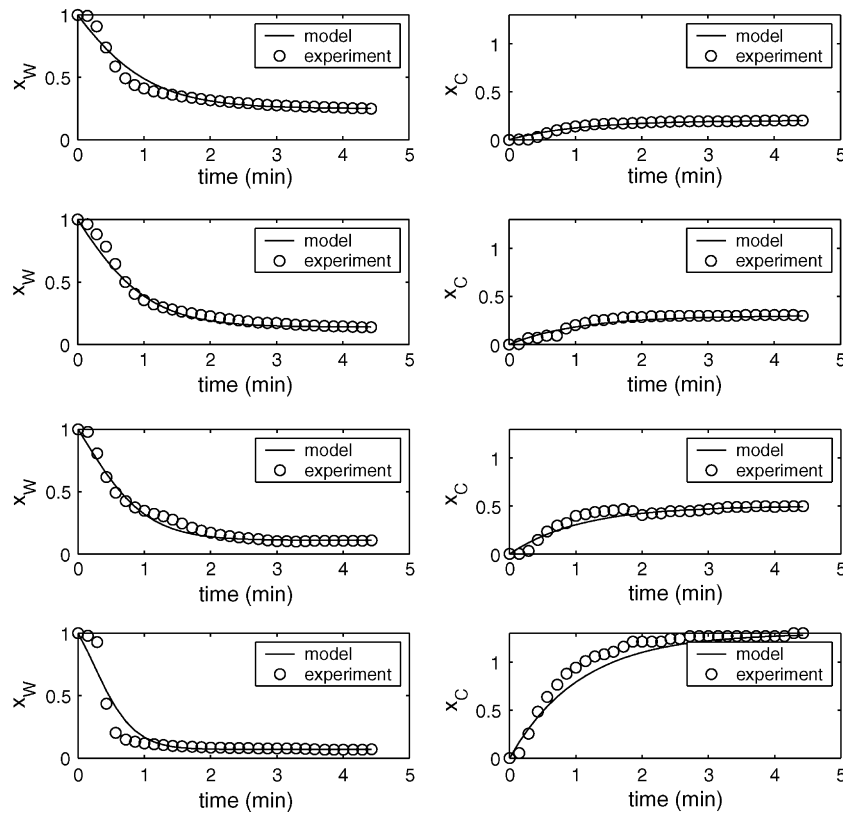


Fig. 6. Results for experimental runs 1–4 as shown in Table 1, performed with different cleaning agent concentrations.

pH can be found in Fig. 5. From the collected volume fractions, the cleaning time can be calculated by $t = V/A_m J$, in which $A_m = 0.07 \text{ m}^2$ and $J = 1501 \text{ h}^{-1} \text{ m}^{-2} = 2500 \text{ ml min}^{-1} \text{ m}^{-2}$. The system has a dead time of $\tau_d = 1.14 \text{ min}$ which corresponds to a dead volume of approximately $V_d = 200 \text{ ml}$ (see Fig. 5).

4. Results

Six experimental cleaning runs were performed at different sodium hydroxide concentrations. Table 1 shows the settings and the effectiveness of the cleaning experiments. Runs 1–4 are

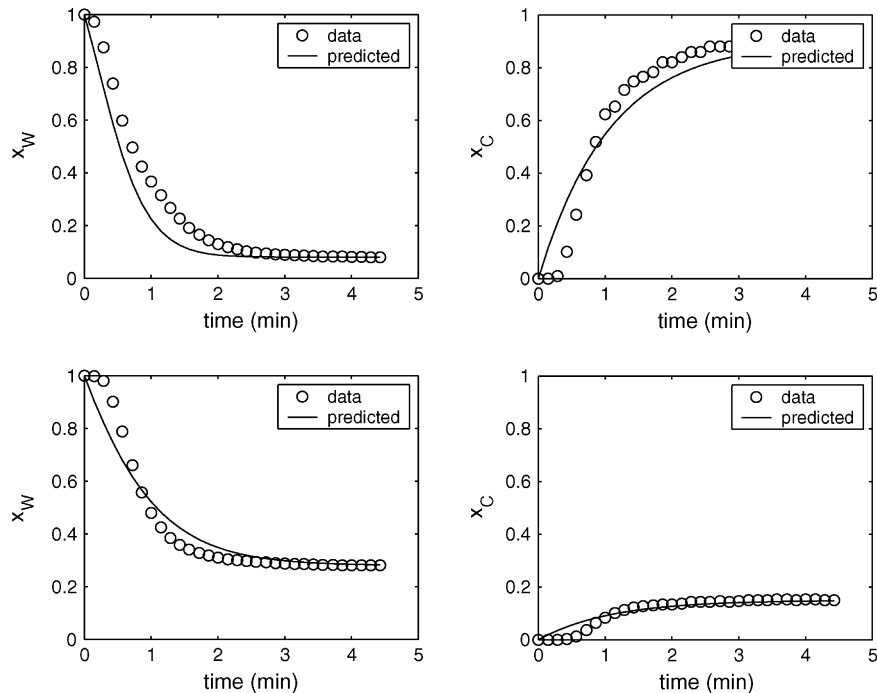


Fig. 7. Fits for the model with estimated parameters for runs 5 and 6 as shown in Table 1.

Table 1
Settings and effectiveness of the cleaning experiments

Run	$x_{C,in}$	J	ϵ_{∞}	$x_{W,\infty}$
1	0.20	1.00	0.75	0.25
2	0.30	1.00	0.86	0.14
3	0.50	1.00	0.89	0.11
4	1.30	1.00	0.93	0.07
5	0.90	1.00	0.92	0.08
6	0.15	1.00	0.72	0.28

used to determine the model parameters, using a nonlinear least squares algorithm. The model parameters were determined to be $k' = 0.93 \text{ min}^{-1}$, $k'' = 2.90 \text{ min}^{-1}$, $n_C = 2.5 \times 10^{-6}$. The value n_C is small, which implies that the cleaning agent is not consumed during the cleaning reaction, which is in agreement with the observations. The comparison of the experimental data and the model for the first four experimental runs is shown in Fig. 6. In order to validate the model, two additional experimental runs were performed with concentrations close to the maximum and minimum allowed sodium hydroxide concentrations. Runs 5 and 6 were used to validate the model and are plotted in Fig. 7. The model fits are calculated according to

$$\text{FIT} = \left(1 - \frac{\text{var}(y - \hat{y})}{\text{var}(y)} \right) \times 100\% \quad (10)$$

where y are the experimental values and \hat{y} are the predicted values. The fits for run 5 are for x_W 95.60% and x_C 93.74%. For run 6 the fits are for x_W 94.44% and for x_C 89.74%.

5. Conclusions

A simple cleaning model, based on component balances was proposed. The model predicts the irreversible fouling decay as function of cleaning time and cleaning agent concentration. The

model parameters can be determined by a simple experimental protocol, measuring trans membrane pressure, pH and turbidity. The execution of the protocol can be done relatively fast, which facilitates frequent online adaptation of the model parameters, when process conditions and water quality vary with time. Experimental verification showed that the model predicts well.

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